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ABSTRACT

Several areas of advanced research related to sampling, analysis, and human exposure assessment of exhaust emission in ambient air have been developed. These include studies of new methods for volatile organic compounds (VOCs), and the development and application of personal exposure monitors (PEMs) in screening for polynuclear aromatics (PNAs) and carbon monoxide (CO). These new methods for screening PNAs are fast, economical, and accurate. The more expensive and time-consuming traditional methods of analysis may be judiciously applied to those samples which the screening methods indicate are high in PNAs. Carbon monoxide, an emission product directly related to automotive emissions, is being monitored using personal exposure monitors in urban scale studies to obtain data on population exposures on a real time basis. Such data may ultimately be used in assessing more accurately human exposure to mobile source and other emissions.

INTRODUCTION

Currently, exposure assessment is made utilizing fixed site monitoring and the results are extrapolated to the general population. Personal exposure monitoring is essential in order to better assess exposure of the population to various pollutants. Presently, a personal exposure monitor for carbon monoxide is available. In order to advance personal monitoring for other pollutants such as volatile organic compounds and polycyclic organic compounds, research is being conducted on solid sorbents for improved sampling of VOCs and analytical methodology for rapid screening of PNAs.

ADVANCES IN SAMPLING: SOLID SORBENTS FOR VOC'S

Although TENAX-GC has been considered the polymer of choice for air sampling, it has poor adsorptive capability for certain low molecular weight polar compounds, e.g., aldehydes, nitrites and amines.

The initial new solid sorbent development was performed at North Carolina State University (NCSU) under an EPA grant (1). The sorbent copolyamide, COP III, was developed. It has a primary amine and double bonding which increases its affinity for polar volatile organics. These properties also resulted in COP III adsorbing excessive amounts of water which makes this sorbent unacceptable. A second sorbent, Thermid 600, was reacted with bisphenol A resulting in a polyimide ether with these characteristics: 1) packs well, 2) thermally stable, 3) low water absorption, and 4) high breakthrough volume. This polar porous polymer is considered useful for trapping both polar and non-polar compounds.

The second phase of the solid sorbent development was conducted at the Research Triangle Institute (RTI) (2) where many aromatic polyimides were synthesized with the objective of finding a solid sorbent or sorbents that collect VOCs in ambient air. Four polyimides met the study objectives and will be further tested.

1. 2,6-dichloro-p-phenyline-diamine
2. 3,3',5,5'-tetra-methyl-benzidene
3. bis-4-amino-phenyleneone
4. bis-4,4'-diamino-diphenyl-methane

These four polyimides and the one polyimide ether (Thermid 600 reacted with bisphenol A) will be evaluated by Battelle Columbus Laboratories (3).

ADVANCES IN ANALYTICAL METHODS: SCREENING METHODS FOR PNA'S

Environmental assessment studies require characterization of PNAs in large numbers of samples over extended periods. Gas chromatography-mass spectrometry (GC/MS) and high performance liquid chromatography (HPLC) have demonstrated their capability to provide specific information for samples containing complex mixtures of pollutants. The GC/MS and HPLC methods, however, require sophisticated and expensive instrumentaion and elaborate experimental procedures. Two techniques, synchronous luminescence (SL) and room temperature phosphorescence (RTP), developed at Oak Ridge National Laboratory have been applied to the work place atmosphere, but are considered adaptable for use in routine screening of atmospheric samples and PEMs (4).

The SL method is a new approach in luminescence spectroscopy. Whereas conventional luminescence measurements are conducted using either a fixed excitation wavelength or a fixed emission wavelength, an SL measurement is based on scanning both emission and excitation wavelengths while maintaining a constant wavelength interval. As a result, the emission bands from individual components in a complex mixture become better resolved in an SL spectrum than in conventional luminescence spectra.

The RTP technique is based upon the detection of the phosphorescence emission from organic compounds adsorbed on a filter paper disc impregnated with a heavy-atom chemical mixture. Unlike conventional phosphorimetric procedures, the RTP technique does not require low-temperatures, refrigerants and cryogenic equipment. The main advantages of the RTP technique include simplicity, rapidity, and cost-effectiveness.

The merits of using SL and RTP as screening techniques for analysis of field samples were examined. These two methods were evaluated in conjunction with traditionally accepted methods of thin layer chromatography (TLC), HPLC, and GC/MS (5).

The two field tests used to evaluate SL and RTP were:

1. An exposure assessment in a wood-burning community, Petersville, Alabama, was conducted by the Tennessee Valley Authority. This study involved outdoor monitoring with the collection of daily total suspended particulates (TSP) and samples collected by dichotomous samplers at two sites.

2. An exposure assessment in a wood-burning community, Waterbury, Vermont, was conducted by Harvard University. This study involves indoor and outdoor monitoring with the collection of respirable particulate samples, TSP and samples collected by dichotomous samplers.

The collected samples from both of the above studies were extracted with dichloromethane (DCM) and sent for PNA analysis to: 1) Oak Ridge National Laboratory for SL and RTP analysis, 2) PEDCo Environmental for GC/MS analysis, and 3) Rockwell International for TLC and HPLC analysis.

Tables 1 and 2 show the relative ranking of total PNA content by SL and RTP. Both SL and RTP, as a rule, were consistent in their ranking of PNAs and generally agreed with independent conventional PNA analytical methods. These results suggest that both SL and RTP will provide good screening techniques which may be applicable to future use in PEMs.

TABLE 1. ORNL RANKING USING SL WITH $\Delta\lambda$=3nm

PEDCO SAMPLE	358-362nm	405-406nm	436nm	471-473nm
654	23	71	183	42
543	7	25	35	12
626	5.5	22.5	31.5	23
547	5	22	16	6
634	4	13.5	20	9
573	8	6	6	7
656	4	4	4.5	4.5

Relative Weighted Peak Heights in Above Wavelengths Range Using a Dilution of 1:10.

PNA CONTENT RANKING

654>543>626>547>634>573>656

TABLE 2. ORNL RANKING USING RTP EMISSION AND EXCITATION AT λ=340nm and λ=390nm

SAMPLE	λ=340nm	λ=390nm
654	227.5	112
543	255	93
547	203	71
634	117	40
626	108	33
573	62	20
656	32.5	11

Heavy Metal Used - Tl/Pb Mixture (Saturated)
Above Numbers Indicate Average Peak Heights of Two Determinations.

PNA CONTENT RANKING

654>543>547>634>626>573>656

ADVANCES IN EXPOSURE ASSESSMENT: PERSONAL EXPOSURE MONITORING

Advances in personal monitoring for exposure assessment studies are currently dependent upon the development of reliable analytical techniques and instrumentation applicable to PEMs. Currently PEMs for carbon monoxide are the most highly developed and evaluated. Personal exposure monitors for CO are being used in urban studies to obtain population exposure data on a real time basis. This information can be used in risk assessment.

A study to evaluate the concept of exposure monitoring using CO PEM's was conducted in Los Angeles utilizing nine participants (6). The results showed that it was possible to measure individual CO exposures and that the concentration did not correspond to data reported by fixed sites in that geographical area. A second exposure study was designed to encompass four cities of different geographical and topographical features (7). The four cities were Los Angeles, Phoenix, Denver, and Stamford. This study was conducted in each city during the winter season when CO would be at its highest concentration. General Electric Model CO-I was the PEM selected for this study because of ruggedness and reliability displayed in the Los Angeles study. Lack of agreement was found between the concentration values at the fixed site monitors and the PEMs. It was found that certain activities could be identified by personal exposure concentration. Three basic activities identified were residential, indoor, and commuting. The results of the fixed sites vs. PEMs by hourly average concentration ranges in each of these activities are shown in Figures 1, 2, and 3. In all cases, the PEM indicated more exposure to CO in excess of the hourly or daily standard than did the fixed site data.

Based on this evidence, an urban scale population exposure program was designed as follows:

1. To develop a methodology for measuring CO exposures of a representative sample of the population of an urban area, for use in exposure assessment.

2. To test, evaluate, and validate this methodology in field studies in Denver, Colorado (8,9) and in Washington, D.C. (8), two urban areas with different ambient pollution levels.

DENVER
GROUP–RESIDENTIAL

FREQUENCY BLOCK CHART

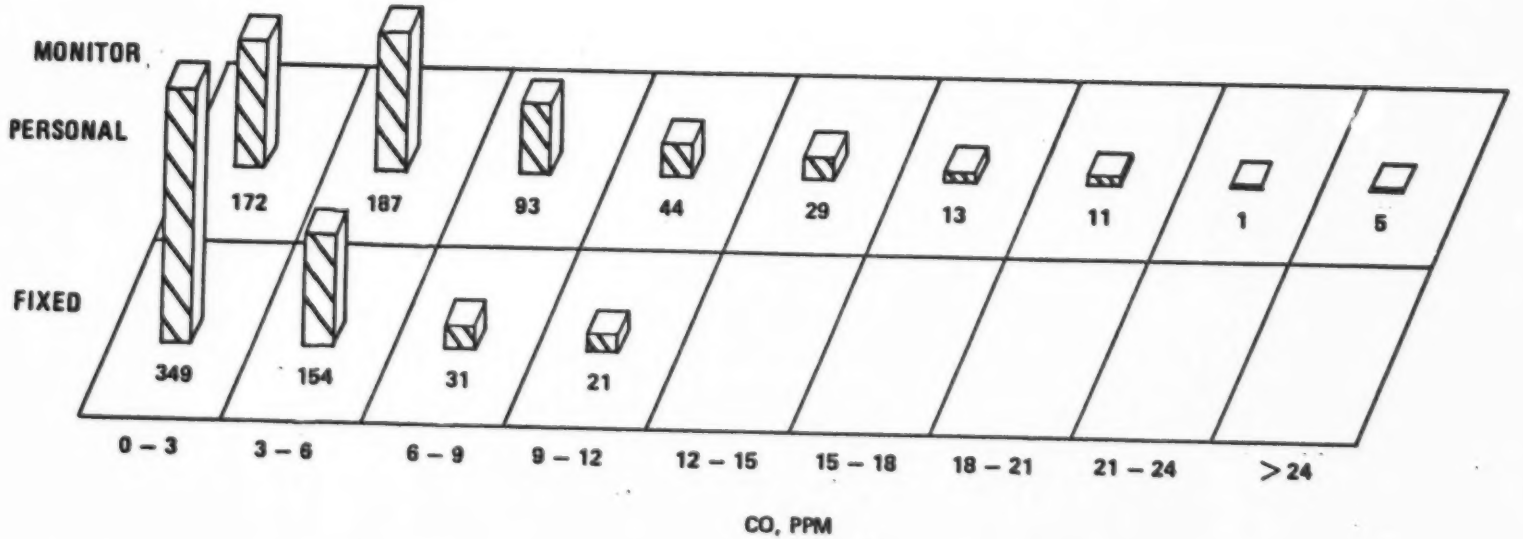

FIGURE 1. COMPARISON OF FIXED SITE AND PERSONAL MONITOR DATA FOR DENVER, COLORADO – AMBIENT DATA

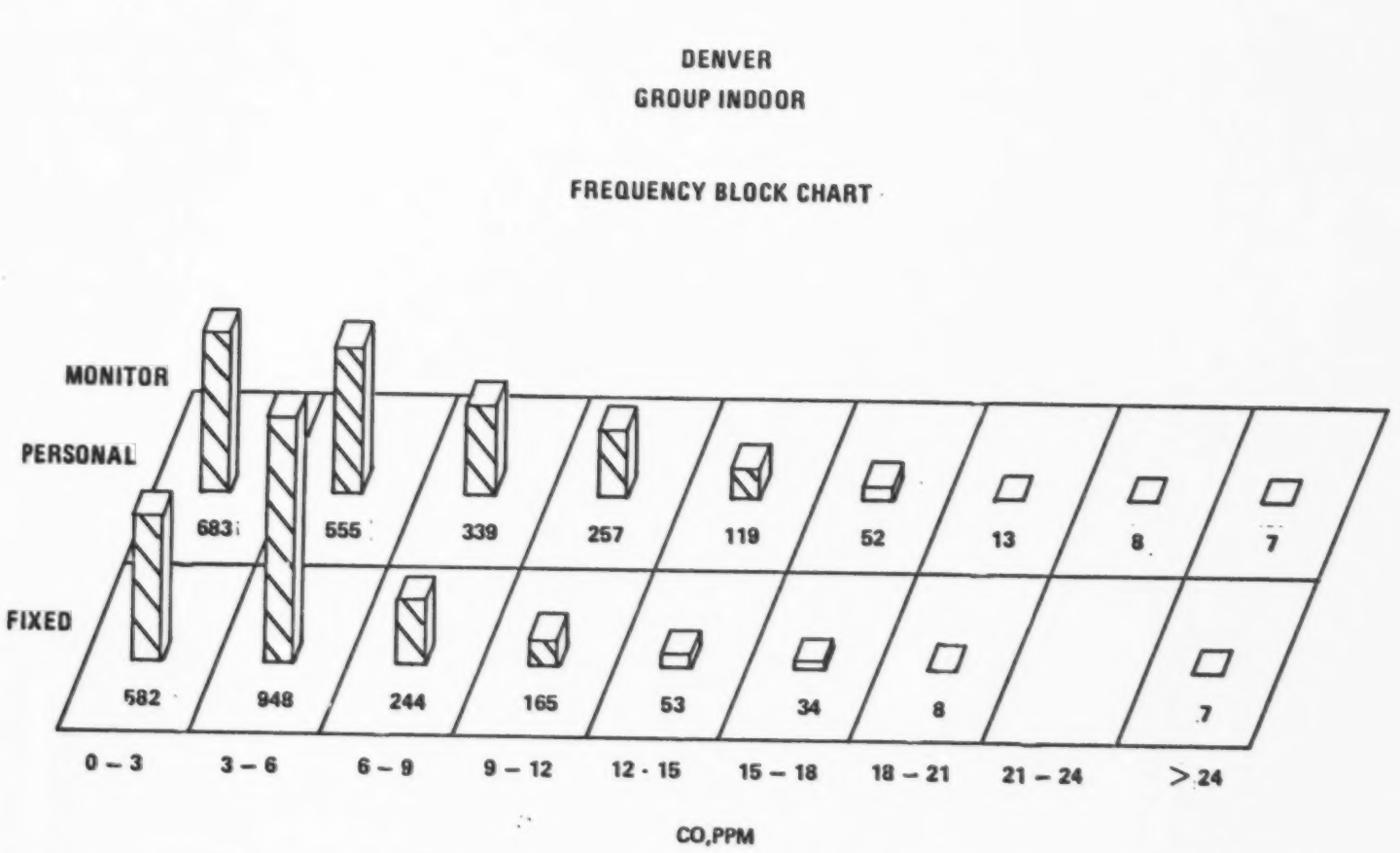

FIGURE 2. COMPARISON OF FIXED SITE AND PERSONAL MONITOR DATA FOR DENVER, COLORADO – INDOOR DATA

DENVER

GROUP–COMMUTING

FREQUENCY BLOCK CHART

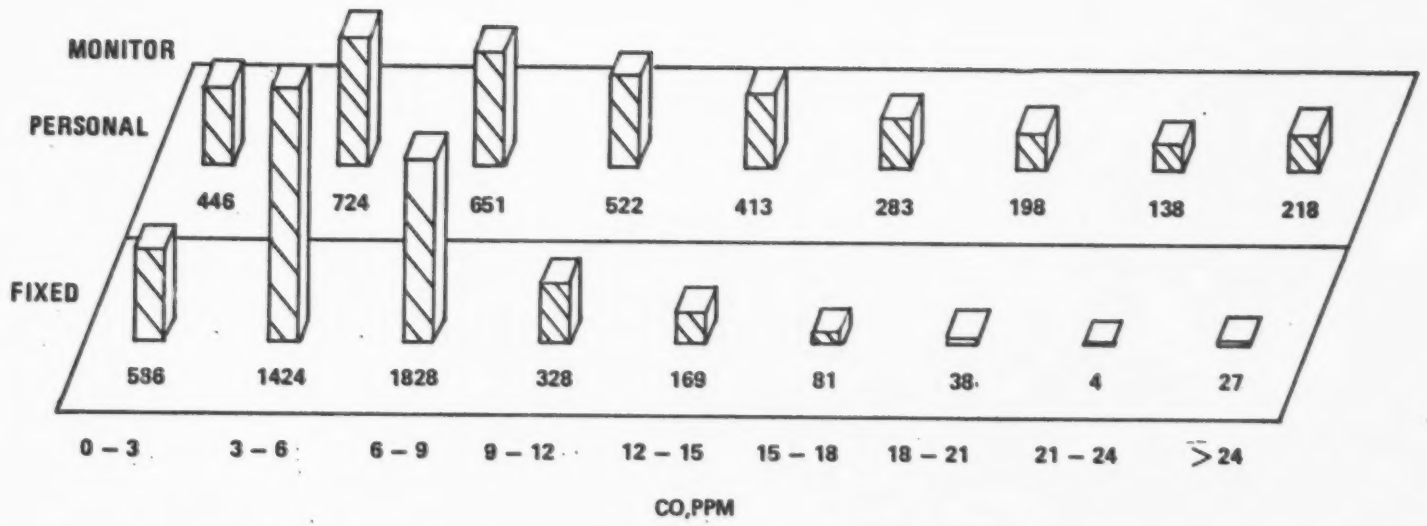

FIGURE 3. COMPARISON OF FIXED SITE AND PERSONAL MONITOR DATA FOR DENVER, COLORADO – COMMUTING DATA

3. To collect data suitable for use in EPA computer models relating CO exposures to personal activities.

4. To collect additional fixed-site data for purposes of comparison with personal monitoring as well as with the designated fixed site air monitoring data.

Two large personal exposure studies are to be carried out in Denver, Colorado and Washington, D.C. between October 1982 and February 1983. 1000 persons in Washington, D.C. will carry a combined CO monitor-data logger for one day. In Denver, 500 persons will carry the instrument for two consecutive days. Participants will log their activities and give a breath sample at the end of the exposure period. The data will be analyzed to relate CO exposures to activities, compare CO exposures to alveolar CO concentrations, and compare CO exposure to ambient CO measurements.

CONCLUSIONS

Recent advances in EPA's monitoring and methods development research have improved through personal exposure monitoring. The availability of personal carbon monoxide monitors has facilitated EPA's first large scale urban personal exposure monitoring studies relating exposure to individual activities in minutes. These studies will provide a data base for evaluating the utility of personal monitoring in comparison to fixed site exposure monitoring. Future studies to evaluate personal exposure to organic compounds (e.g., VOCs and PNAs) will depend upon the development of sampling and analytical methodologies applicable to the development of PEMs for organics. The PNA screening method employing filter paper impregnated with heavy metals and analysis by RTP or SL may provide such a personal PNA monitor for future assessment of human exposure.

REFERENCES

1. U.S. Environmental Protection Agency, Grant No. CR-807922-01-1: 1980-1981, "Porous Polymer-Adsorption of Volatile Organic Toxicants in Ambient Air. The Synthesis and Evaluation of Aromatic Copolymides Containing N-Propargyl Groups."

2. U.S. Environmental Protection Agency Contract No. 68-02-3440: 1982, "Preparation and Evaluation of New Sorbents for Environmental Monitoring."

3. U.S. Environmental Protection Agency Contract No. 68-02-3847, Work Assignment 15: 1982, "Evaluation of Solid Sorbents for the Collection of Volatile Organics from Ambient Air."

4. Vo-Dinh, T.: 1982, Second Annual National Symposium on Recent Advances in Measurement of Pollutants in Ambient Air and Stationary Sources, "A Personal or Area Dosimeter for Polynuclear Aromatic Vapors," in press.

5. U.S. Environmental Protection Agency Contract No. 68-02-3496, Work Assignment 21: 1982, "Analysis of Air Samples and Field Test of the Synchronous Luminescence and Room Temperature Phosphorescence Methods."

6. U.S. Environmental Protection Agency Contract No. 68-02-3412: 1981, "Pilot Field Study - Carbon Monoxide Exposure Monitoring in the General Population."

7. U.S. Environmental Protection Agency Contract No. 68-02-3173, 68-02-3168, 68-02-3629, 68-02-3412 (report is compilation of four separate contractual efforts): 1982, "Carbon Monoxide Concentrations in Four U.S. Cities During the Winter of 1981," in press.

8. U.S. Environmental Protection Agency Contract No. 68-02-3679: 1982, "Study of Exposure to Carbon Monoxide of Residents of Washington, D.C. and Denver, Colorado."

9. U.S. Environmental Protection Agency Contract No. 68-02-3755: 1982, "Carbon Monoxide Exposure in Denver, Colorado."